# Cummins-ORNL\FEERC Emissions CRADA:

# $NO_x$ Control & Measurement Technology for Heavy-Duty Diesel Engines,

## *Self-Diagnosing SmartCatalyst Systems*

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Project ID:
ACE032

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U.S. DOE Program Management Team:
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***This presentation does not contain any proprietary, confidential, or otherwise restricted information.***

# Overview

## Timeline

- Current SOW started FY13
- SOW extends through FY15
- New 3-year SOW submitted

## Barriers

- *From DOE VT MYPP:*
  - 2.3.1.B: Cost-effective emission control
  - 2.3.1.C: Modeling for emission control
  - 2.3.1.E: Emissions-control durability

## Budget

- 1:1 DOE:Cummins cost share
- DOE Funding:
  - FY2013: $400k
  - FY2014: $350k
  - FY2015: $283k

## Partners

- **ORNL & Cummins Inc.**
- CLEERS
- Chalmers
- Politecnico di Milano
- Queen’s Univ. Belfast
- Univ. of Chem. & Tech. Prague

# Objectives & Relevance

***Improve Catalyst Models, Design & Control***

for Enabling Emissions Compliance & Improved Fuel Economy

**Objectives**

- Develop diagnostics to advance applied & basic catalyst insights
- Understand impact of ageing on catalyst performance
  - Focus on distributed & transient performance
  - Correlate functional impacts: SCR, $NH_3$ capacity & oxidation reactions
- Identify strategies for catalyst-state assessment
- Apply data to improve & critically assess catalyst models

**Relevance – Detailed Catalyst Insights impact:**

- Improve dynamic catalyst models
- Improve control strategies & design model-based controls
- Optimize $NH_3$ dosing control for fuel economy and overall fluid economy
- Reduce required engineering margins (engine-efficiency vs. emissions tradeoffs)
- Reduce system capital & operation costs

# Milestones

**2014 Milestones:**

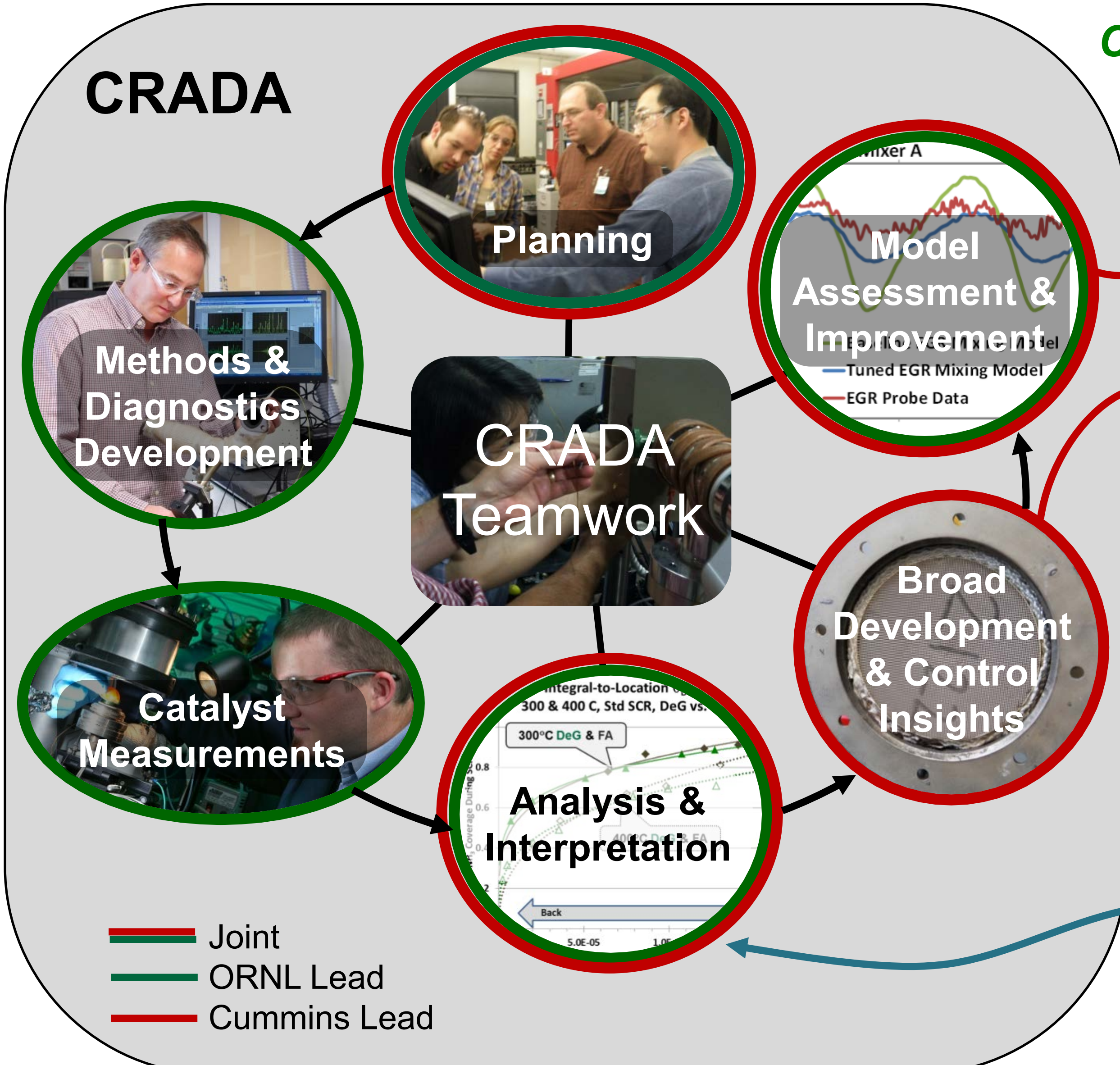
- ✓ **Q1:** Complete assessment of probe-to-probe variations in $NH_3$ sensors
- ✓ **Q2:** Assess $NH_3$ capacity of Lab-Aged 2010CMI sample
- ✓ **Q3:** Assess distributed performance of Lab-Aged 2010CMI sample
- ✓ **Q4:** Compare distributed performance of DeGreened & Lab-Aged 2010CMI

**2015 Milestone (on schedule for timely completion):**

- ✓ **Q2:** Assess distributed performance of Field-Aged commercial SCR catalyst
- **Q3:** Present CRADA ageing insights at CLEERS Workshop

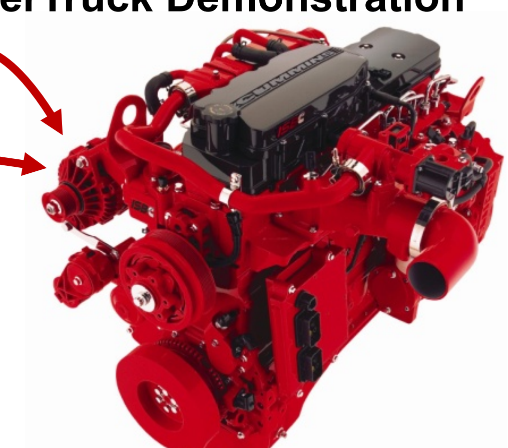
# Approach

## *Spatiotemporal Intra-Catalyst Characterization*
for Fundamental & Practical Insights
to Enhance Performance, Control, Cost & Durability




***Clean, Fuel-Efficient, Durable***
**Engines in the Marketplace**

**6.7L ISB (Dodge Ram)**
**ISV5.0 (Nissan Titan)**
**SuperTruck Demonstration**

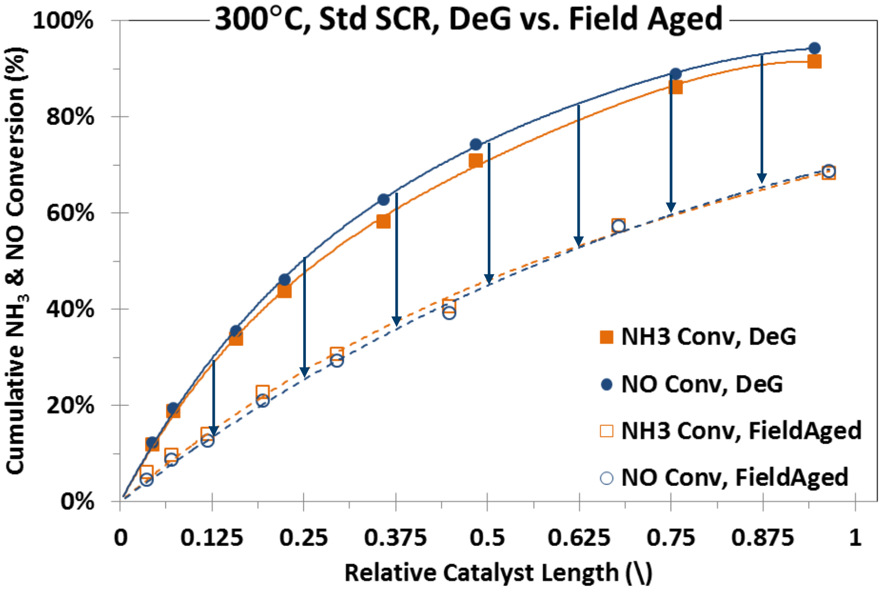


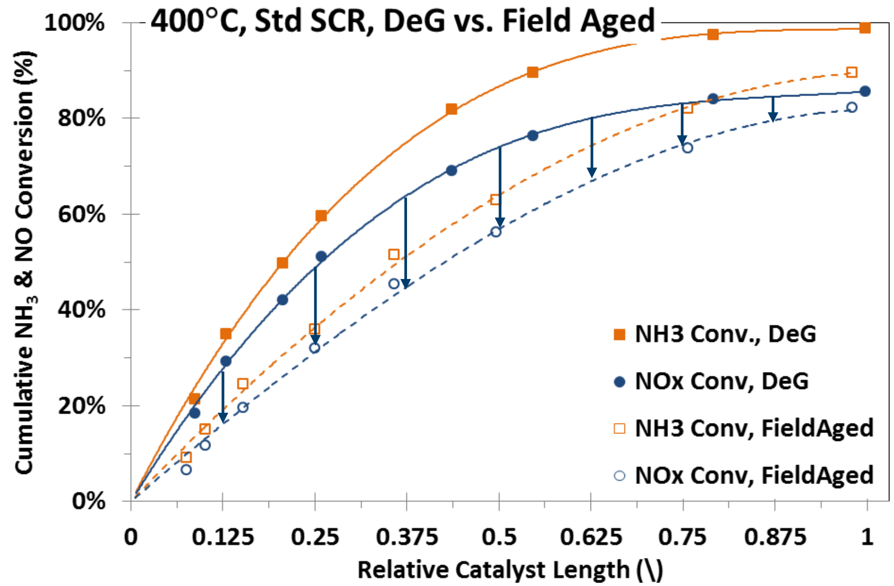
# Technical Progress: *Summary*

- **Background: from FY12 & 14 Project Years** ***(responding to Reviewer Feedback)***
  - Commercial & Model Cu-SCR catalysts investigated with multiple collaborators
  - Distributed Capacity dictated by Adsorption Isotherm & Local [$NH_3$]
  - SCR kinetic parameters determined from intra-SCR distributed data
    - under normal operating conditions & distributed model published (with Chalmers)
  - Analytical SpaciMS development
    - Improved analysis, Fast SpaciMS & demonstrated non-invasive Spaci nature
  - Multiple University collaborations: Chalmers, UCT Prague, PoliMi, QUB, MI Tech

- **FY15 work focused on a Field Aged Commercial 2010CMI SCR**
  - Distributed performance: NO & $NH_3$ conversion, $NH_3$ oxidation & capacity
  - Objective: understand how Field Ageing impacts catalyst functions & performance
  - Correlate functional impacts of Field Ageing relative to DeGreened performance
    - DeGreened sample: **DeG**
    - Hydrothermally Aged sample: **HTA**
    - Field Aged sample: **FA**
  - Assess catalyst models against spatially resolved data
  - Gain insights regarding catalyst-state assessment

# Tech.Prog.: Field Ageing Significantly Reduces SCR Conversion




## Commercial SCR Sample

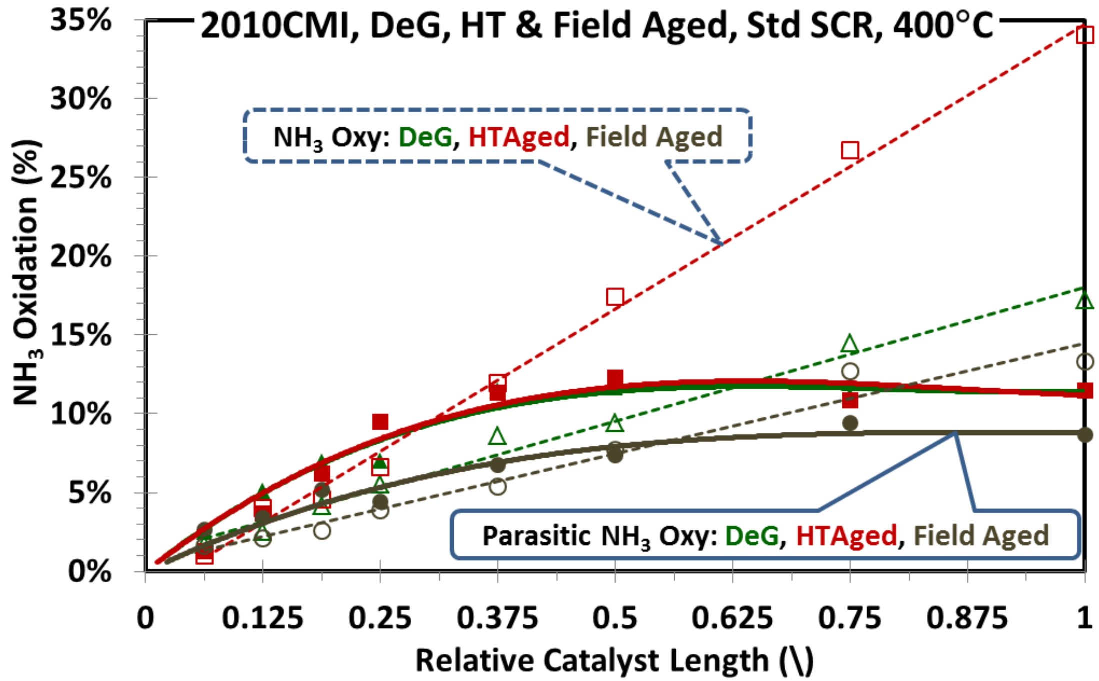
- 2010CMI, Cu-SAPO-34
- Field Ageing
  - Sample from real-world use
  - Normal ageing profile
- Previous work focused on DeG & HTA

- Major SCR degradation in front half
  - ~40-55% lower conversion at 300°C
  - ~20-40% lower conversion at 400°C
- Parasitic $NH_3$ Oxidation
  - negligible at 300°C
  - apparent at 400°C for both DeG & FA

***Identify Specific Parameters Impacting SCR Loss with Field Ageing,***

***Focus on Parameter-Performance Correlations & Model Comparisons***

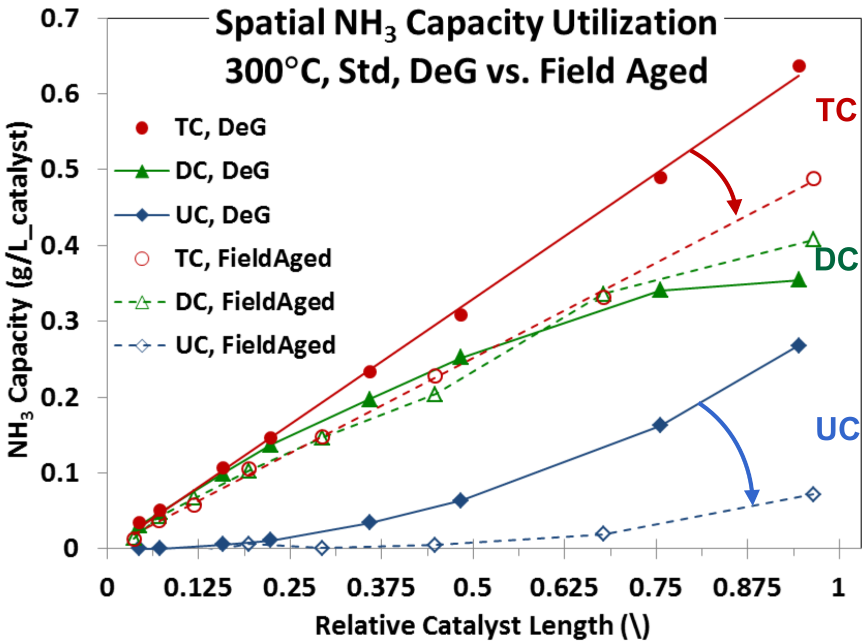
# Field Ageing Reduces both Parasitic & $NH_3$ Oxidation




- Parasitic $NH_3$ Oxidation: PO (during SCR)
  - FA ~20% lower than DeG
    - Reduced competition should cause greater SCR conversion if PO limits SCR
  - HTA ~same as DeG
- $NH_3$ Oxidation (in absence of $NO_x$)
  - FA ~20% lower than DeG
  - HTA ~100% greater than DeG

- ***FA & HTA have different impacts***
- ***FA SCR loss >> PO loss***
  - ***Significant PO change would cause opposite SCR trend***
- ***FA reduces both SCR & PO***
  - ***FA apparently impacts a common site***
  - ***SCR is more sensitive to this impact***
  - ***PO site competition not limiting SCR***

# Tech.Prog.: Field Ageing Changes TC & UC, but Little DC Impact




Total $NH_3$ Capacity: **TC**

Dynamic $NH_3$ Capacity: **DC**

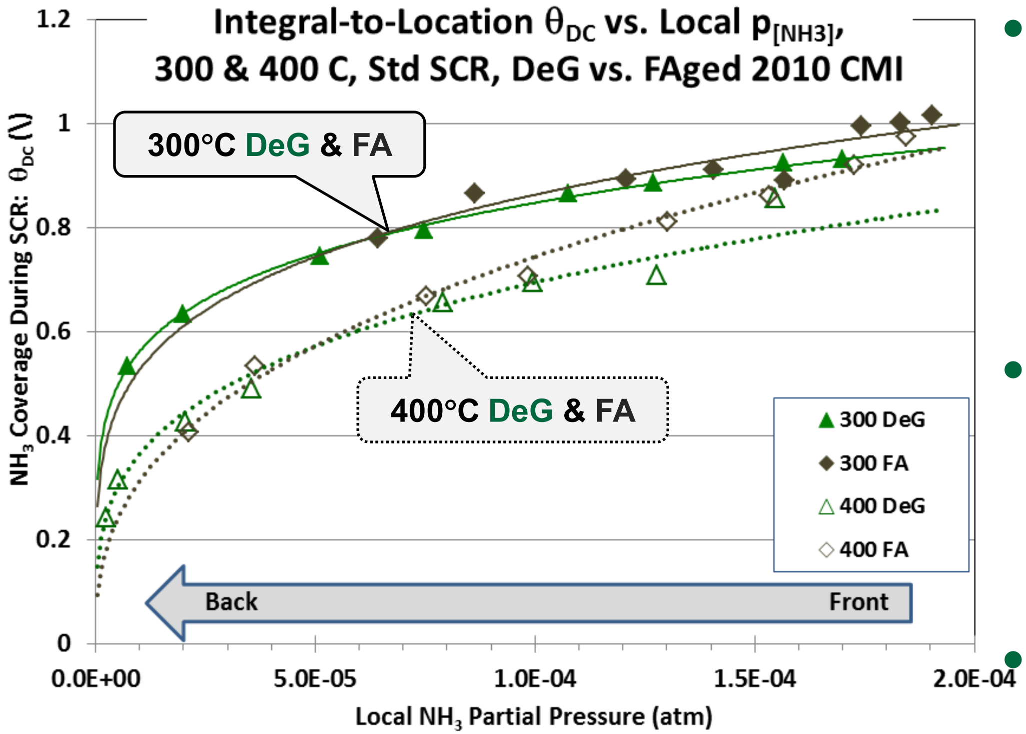
- **DC: fraction used during SCR**

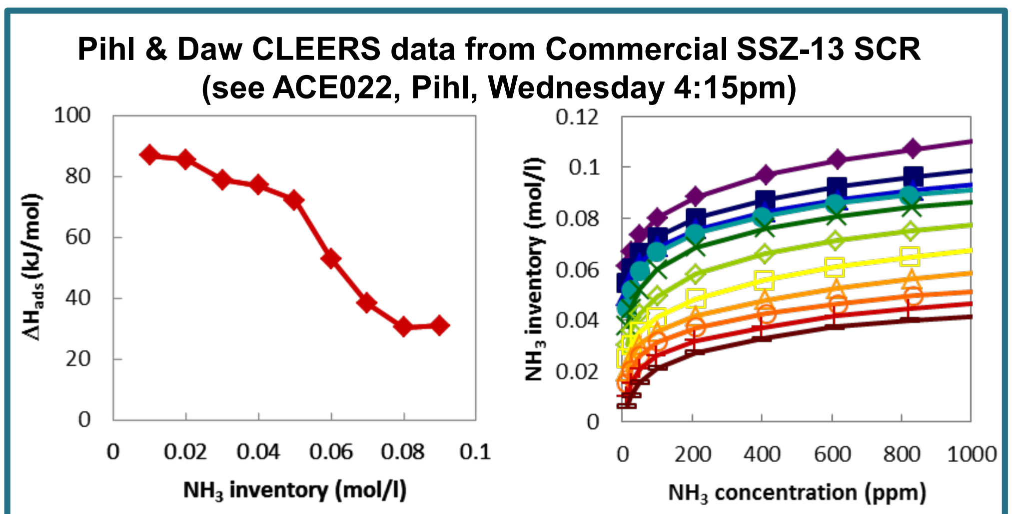
Unused $NH_3$ Capacity: **UC**

**DC + UC = TC**

- Total $NH_3$ Capacity: **TC**
  - FA TC~25% lower at both 300 & 400°C
- Dynamic $NH_3$ Capacity: **DC**
  - DC≈TC at catalyst front
  - FA causes DC≈TC deeper into catalyst
    - DC saturated deeper into catalyst
    - ***Overall very small DC change***
    - [$NH_3$] similar at DC-TC separation point
      - Suggests similar Adsorption Isotherm
- Unused $NH_3$ Capacity: **UC**
  - FA lowers UC (Due to TC & DC behavior)
    - May impact dosing control
    - Candidate for catalyst-state monitor
- Same general behavior at 400°C
- ***FA has little impact on DC quantity***
- ***FA SCR loss >> DC change***
  - ***Apparently not due to DC quantity loss***
  - ***But, is FA DC less accessible?***

# Tech.Prog.: Field Ageing Does Not Change $NH_3$ Adsorption Energetics




- $NH_3$ Isotherm from SpaciMS data
  - Normalized coverage shown
  - Under SCR reaction conditions
  - Adsorption is much faster than even Fast SCR (previously shown)
- Shape is like 2-site Langmuir
  - See Pihl & Daw CLEERS data
    - From commercial SSZ-13 SCR
  - Distinct knee at low $NH_3$ partial pressure
- Isotherm is same at a give temperature
  - Shape would change with energetics
    - e.g., if selective adsorption-site impact
  - Isotherm flattens at higher temperature
    - Typical nature for Langmuir isotherm
- Simplifies modeling of aged samples
  - Field ageing reduces number of sites
  - But adsorption occurs in same way
  - ***Use same model with scaling factor***

## Tech.Prog.: Summary of Field-Ageing Impacts on SCR Functions

| Function | Field-Ageing Impact vs. DeGreened | |
|---|---|---|
| | 300°C | 400°C |
| SCR | **40-55% lower** | **20-40% lower** |
| Parasitic $NH_3$ Oxidation | **NA; same** | **20% lower (opposite trend)** |
| $NH_3$ Oxidation | NA; same | 20% lower |
| $NH_3$ Inhibition limit | same | same |
| Total $NH_3$ Capacity | 25% lower | 25% lower |
| Dynamic $NH_3$ Capacity | **ca. same** | **ca. same** |
| Unused $NH_3$ Capacity | lower | lower |
| $NH_3$ Adsorption Energetics | same | same |

- Results generally consistent with
  - FA reduces TC & impacts common site related to SCR & PO
  - Practically nonselective FA impact on $NH_3$ adsorption-site energetics
  - DC quantity and PO competition not limiting FA SCR
  - FA may make DC less accessible, causing longer\slower SCR
- Additional catalyst characterization needed
  - Cu sintering
  - Poisoning; e.g., by lube components (S, Zn, P, Ca)
  - Number & nature of surface sites
- Comparison to Cummins catalyst models is ongoing

# Responses to 2014 Review Comments

**FY2014 AMR Review**
**(7 Reviewers; max score: 4)**

| Category | Score |
|---|---|
| Approach | 3.50 |
| Tech Progress | 3.07 |
| Collaboration | 3.50 |
| Future Research | 3.21 |
| **Weighted Average** | **3.25** |

## Numerous Positive Comments:

- “excellent rating,” “thought-out approach,” “very important project”
- “very interesting,” “good work characterizing various functions”
- “outstanding collaboration,” “excellent group of collaboration partners”
- “characterization of axial changes in $NH_3$ storage is important”
- “development & comparison to ageing models is important”
- “OBD is a major challenge and this work can shed light on this”

## Recommendations:

- Some question re. how intra-SCR spatially resolved information can be used in practice
  - ***Spaci-like analysis provides spatial insights re. functional activity and ageing impacts***
  - ***These insights can guide strategies for practical on-vehicle OBD; even w/o spatially resolved sensing; e.g., see two slides in Technical Backup Slides***
- Some questions re. sufficiency of results given that project started in 2013
  - ***The AMR presentation focuses on the previous year***
  - ***A more detailed multi-year summary has been provided in the Technical Backup Slides***
- Several comments re. Cummins’ contribution & benefits, and contributions of the informal collaborators
  - ***This has been highlighted in the presentation***
  - ***A summary of contributions is provided in the Technical Backup Slides***
- Several comments re. formalizing the non-CRADA collaborators & more in-depth discussion of their work
  - ***The CRADA partners bring knowledge from wide-ranging sources to the project***
  - ***The informal partnerships strengthen the project w/o being exposed to CRADA-protected info.***
  - ***CRADA is a formal CMI-ORNL agreement; the AMR primarily focuses on CRADA-partner work***
- Several suggestions that transient analysis be used to probe spatiotemporal functional interactions
  - ***This was discussed last year, and is being incorporated in the Future Work Plans***

# Collaborations & Coordination with Other Institutions

- **Cummins**
  - CRADA Partner, Neal Currier (Co-PI)
- **CLEERS (ACE022, Pihl, Wednesday 4:15pm)**
  - Diagnostics, analysis & modeling coordination
- **Chalmers (Prof. Olsson)**
  - Kinetic modeling of $NH_3$-SCR
  - Xavier Auvray, et al. (2015), Applied Catalysis B: Environmental 163, 393-403.
- **Politecnico di Milano (Profs. Tronconi & Nova)**
  - Mechanistic SCR studies (**with CLEERS**)
  - Maria Pia Ruggeri, et al. 8th ICEC, 2014.
- **Queen's University, Belfast (Prof. Alex Goguet)**
  - Minimally invasive nature of SpaciMS
  - Alexandre Goguet, et al. (2014). Catalysis Today 236, 206-208.
- **UCT, Prague (Prof. Marek & Dr. Kočí)**
  - $N_2O$ formation studies (**with CLEERS**)
  - David Mráček, et al.  (2015). Appl.Catalysis B: Env. 166-167, 509-517.
  - David Mráček, et al. 2014 CLEERS Workshop.
  - Petr Kočí, et al. 8th ICEC, 2014.
- **Publications, Presentations & Recognition**
  - 3 Archival Journal Publication, 3 Presentations
  - ORNL-Cummins partnership recognized by Dr. Danielson, DOE EERE Assistant Secretary, for enabling clean & efficient engines for current & future vehicles

# Remaining Challenges & Barriers, and Proposed Future Work

| Remaining Challenges: | Future Work (FY16-18): |
|---|---|
| • Robust SCR models that can accurately predict transient distributed performance<br>  - Most critical assessment method | • Compare CMI models to measurements<br>  - Individual function & integrated performance<br>    ▪ Initial focus on $NH_3$ capacity & isotherm<br>  - Mutual guidance: models ↔ experiments |
| • Origin of Field Ageing performance loss | • Catalyst characterization<br>  - Sintering, poisoning, deAl, zeolite structure<br>• Compare models and experiments |
| • Analytical improvements<br>  - Impacts capacity & transient analysis | • Differentiating transient impacts of instrument response and dynamic catalyst changes<br>  - e.g., dynamic catalyst oxidation-state changes |
| • Transient catalyst performance | • Transient response experiments<br>  - Spatial & temporal resolution<br>  - How functions transitions between SS states<br>  - Model assessment<br>  - Analysis for catalyst-state assessment |
| • Other Field-Ageing impacts and catalysts<br>  - Are existing insights broadly representative | • Measurements of other FAged samples<br>• Measurements of other catalyst samples<br>  - With different functional & parameter sensitivities |

# Summary

- **Relevance**
  - CRADA work enables improved catalyst knowledge, models, design & control
  - This reduces catalyst system costs & required engine-efficiency tradeoffs
  - This in turn enables DOE goals for improved fuel economy
- **Approach**
  - Develop & apply diagnostics to characterize catalyst nature
  - Analyze data to understand mechanistic details of catalyst functions & ageing impacts
  - Develop improved catalyst models based on improved catalyst knowledge
- **Technical Accomplishments**
  - Assessed impacts of Field Ageing on commercial SCR catalyst functions
    - $NH_3$ capacity, SCR, Parasitic $NH_3$ oxidation, $NH_3$ Oxidation, Dynamic Inhibition
    - Field Ageing does not change $NH_3$ energetics; i.e., can use same isotherm model
- **Collaborations**
  - Numerous university collaborations resulting in presentations, publications and advances
  - Coordination & collaboration with other DOE projects to maximize benefit
- **Future Work**
  - Apply data & insights to improve catalyst models & catalyst-state assessment
  - Experiments to understand transient catalyst performance
  - Analysis of broader field-aged sample set and catalyst types

# ***Technical Back-Up Slides***

# Overview *(with more Barriers details)*

## Timeline

- New SOW started FY13
- SOW extends through FY15
- New 3-year SOW & goals extension submitted

## Budget

- 1:1 DOE:Cummins cost share
- DOE Funding:
  - FY2013: $400k
  - FY2014: $350k
  - FY2015: $283k

## Barriers

- *From DOE VT MYPP:*
  - 2.3.1.B: Cost-effective emission control
  - 2.3.1.C: Modeling for emission control
  - 2.3.1.E: Emissions-control durability
- *General*
  - *Emissions controls*
    - Catalyst fundamentals & practical insights
    - Catalyst models (design tools & imbedded)
    - Control strategies & OBD
  - Combustion Efficiency
    - Shift emissions tradeoff to fuel efficiency
  - *Durability*
    - Enhanced durability via improved controls
  - *Cost*
    - Lower development, catalyst & sensor costs

## Partners

- **ORNL & Cummins Inc.**
- CLEERS & University collaborators

# Technical Progress: *Summary* (details re. FY12-14 Project Years)

- **Background: from FY12 & 14 Project Years**
  - Multiple SCR catalysts investigated
    - Commercial Cu-SAPO-34; SpaciMS & SpaciIR (with CLEERS & MI Tech)
      - Distributed capacity & SS performance in DeG & HTAged states
    - Model Cu-Beta; (with Chalmers)
  - Distributed Capacity dictated by Adsorption Isotherm & Local [$NH_3$]
    - SCR reaction only changes [$NH_3$] distribution & not isotherm
    - Adsorption equilibrium faster than even Fast SCR
    - Formulation will change isotherm
    - Additional isotherm work ongoing in CLEERS
  - SCR kinetic parameters determined from intra-SCR distributed data
    - under normal operating conditions & distributed model published (with Chalmers)
  - Analytical SpaciMS development
    - Improved analysis, Fast SpaciMS & demonstrated non-invasive Spaci nature
  - Multiple University partnerships: UCT Prague, PoliMi, Chalmers

- **FY15 work focused on a Field Aged 2010 CMI SCR**
  - Distributed performance: NO & $NH_3$ conversion, PO & $NH_3$ oxidation, capacity
  - Objective: understand how Field Ageing impacts catalyst functions & performance
  - Apply to assess catalyst models and gain insights re. state assessment

# Technical Progress: *Summary of Participant Actions*

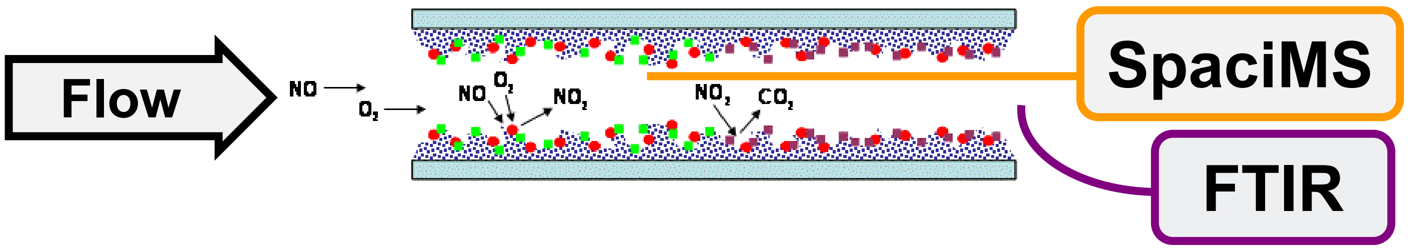
- **Summary of FY15 CRADA Participant Contributions**
  - ***Responding to AMR Reviewer feedback***
  - 1:1 DOE:Cummins cost share; i.e., Cummins matches DOE investment 1:1
  - Supply fresh, HTAged and Field Aged catalsyt samples (CMI lead)
  - Bench reactor analysis of catalyst samples (ORNL lead)
  - Analysis of SpaciMS and other reactor data (ORNL lead)
  - Interpretation of results (Joint ORNL & CMI)
    - Basic insights; limiting conditions, surface chemistry, correlations
    - Practical insights; strategies for catalyst-state assessment
  - Model comparison, assessment and modifications (CMI lead)
  - Next-steps and future-work planning (Joint ORNL & CMI)

  - Informal partnerships outside the CRADA FY13-15
    - *Lead participant is indicated parenthetically*
    - SCR kinetic analysis & modeling with Chalmers
      - Planning (Joint), diagnostics & analysis (ORNL), experiments at ORNL (Joint), modeling (Chalmers)
    - Mechanistic studies with Politecnico di Milano
      - Planning (Joint), diagnostics & analysis (ORNL), experiments at ORNL (Joint), interpretation (Joint)
    - N2O formation studies with University of Chemistry and Technology, Prague
      - Planning (Joint), diagnostics & analysis (ORNL), experiments at ORNL (Joint), modeling (UCTP)
    - SpaciMS studies with Queen's University, Belfast
      - Planning (Joint), diagnostics & analysis (joint), experiments at ORNL (ORNL), modeling (QUB)

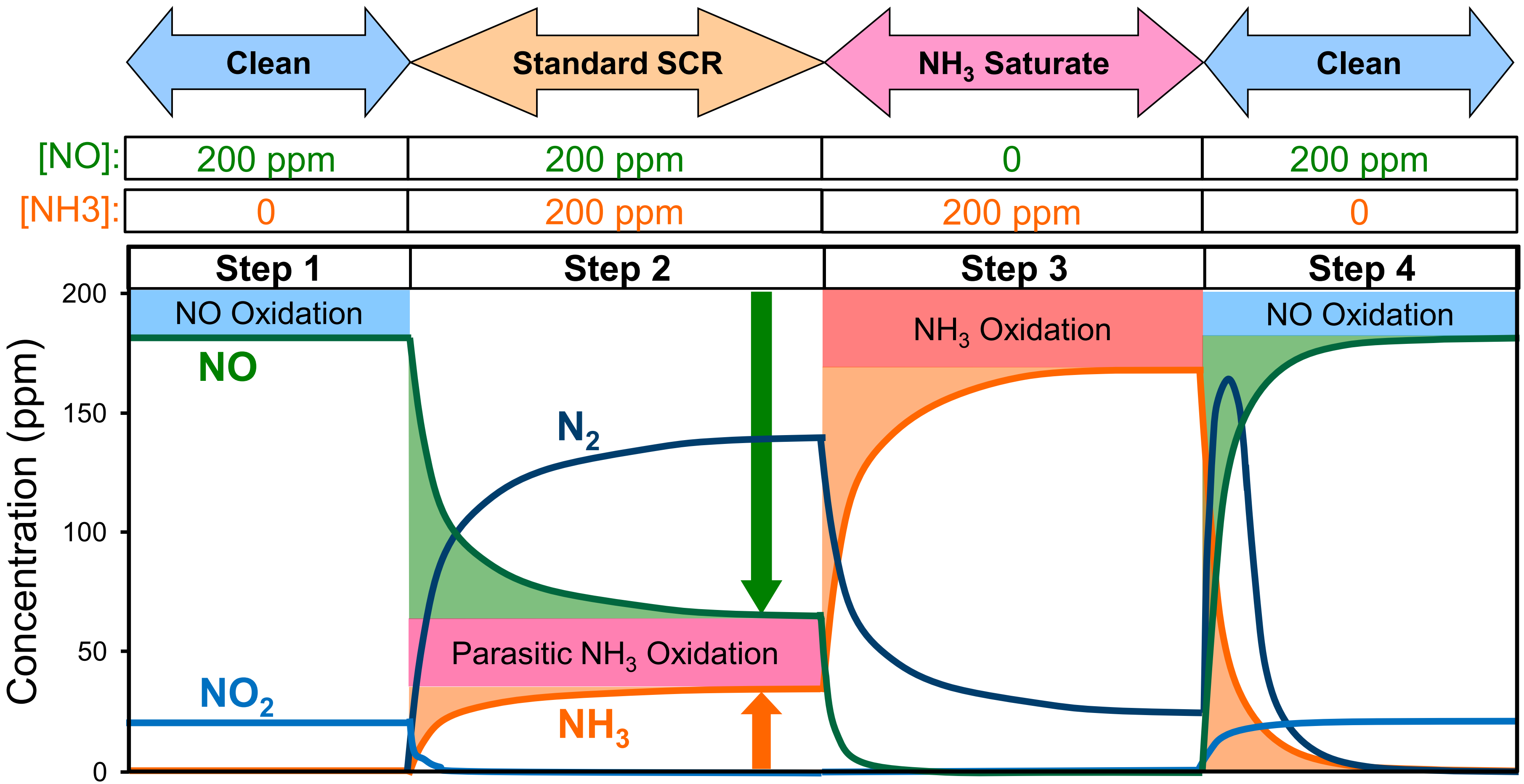
# Experimental: Catalyst, Conditions, Methods & Approach

| | Commercial |
|---|---|
| Catalyst | 2010 CMI, Cu-SAPO 34 |
| Mini-Core size | 21 cells; ca. 2.45-cm long x 0.78 wide |
| Channel density | 300 cpsi |
| Space Velocity | 60,000 $hr^{-1}$ |
| $NH_3$, $NO_x$ | 200ppm, 200ppm |
| Base $O_2$ & $H_2O$ | 10% & 5% |
| Temperatures | 200, 300 & 400°C |
| Standard SCR | ✓ focus of these slides |
| Fast SCR | ✓ |
| Diagnostic | SpaciMS & FTIR |

| State | Conditions |
|---|---|
| DeGreened | 700°C, 4hrs, 10%$O_2$ + 5%$H_2O$; <br>• From front of sample B11-22 |
| Hydrothermal Ageing | 800°C, 50hrs, 14%$O_2$ + 8%$H_2O$; <br>• CMI ageing rig: 10-9-2013 <br>• From front of sample B11-23 |
| Field Ageing | ?; prepared by CMI; <br>• CMI date: 7-1-2014 <br>• From front of larger sample; <br>• Pretreatment at ORNL: <br>  • 500°C to remove HC & S <br>  • Cycling at 200, 300 & 400C to steady state |



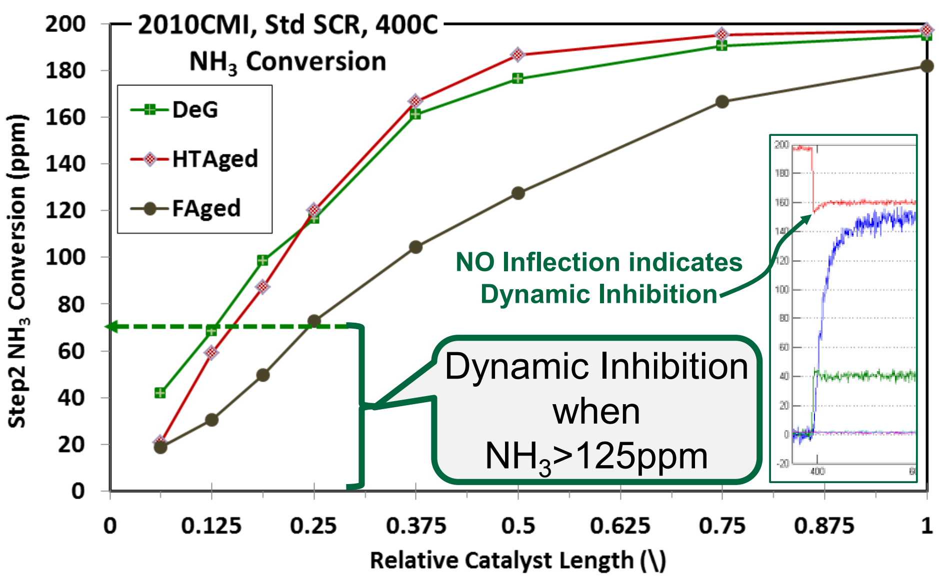
# Cummins 4-Step Protocol Resolves Reaction Parameters




- Step1: NO oxidation
- Step2: SS $NO_x$ & $NH_3$ conversions, Parasitic $NH_3$ oxidation, Dynamic $NH_3$ capacity
- Step3: $NO_x$-free $NH_3$ oxidation, Unused $NH_3$ capacity
- Step4: NO oxidation, Total $NH_3$ capacity

**Total = Dynamic + Unused**

# Tech.Prog.: Field Ageing Does Not Change Dynamic $NH_3$ Inhibition




Tronconi, Cat.Today 105, p529; describes dynamic inhibition

- 'modified redox (MR) SCR rate law'
- Depends on T, $C_{NO}$, $\theta_{NH3}$ & $C_{O2}$

$$r_{NO} = \frac{k'_{NO} O' \exp\left(-\frac{E_{NO}}{RT}\right) C_{NO}\theta_{NH_3}}{1 + K'_{NH_3}\frac{\theta_{NH_3}}{1-\theta_{NH_3}}}\left(\frac{p_{O_2}}{0.02}\right)^{\beta} \qquad (12)$$

- $r_{NO}$: rate of DeNOx reaction
- $E_{NO}$: Activation energy for DeNOx reaction
- $C_{NO}$: gas phase concentration of NO
- $\theta_{NH3}$: surface coverage of $NH_3$
- $k_{NO}$: pre-exponential factor for DeNOx reaction rate constant
- $K_{NH3}$: $NH_3$ rate parameter
- $p_{O2}$: $O_2$ partial pressure
- **S1: redox site for $O_2$ & NO adsorption/activation**
- **S2: acidic site for $NH_3$ adsorption**

- Dynamic inhibition at SCR start
  - Observed in catalyst front for all samples
  - ***Observed above consistent [$NH_3$] limit***
    - ≳ 165ppm [$NH_3$] at 300°C
    - ≳ 125ppm [$NH_3$] at 400°C
      - 400°C more sensitive
      - Due to faster reaction or less accessible DC?
      - More sensitive to spillover from Higher-E S2 sites, which are more dominant at high-T
  - Impacts NO & $NH_3$ adsorption parameters

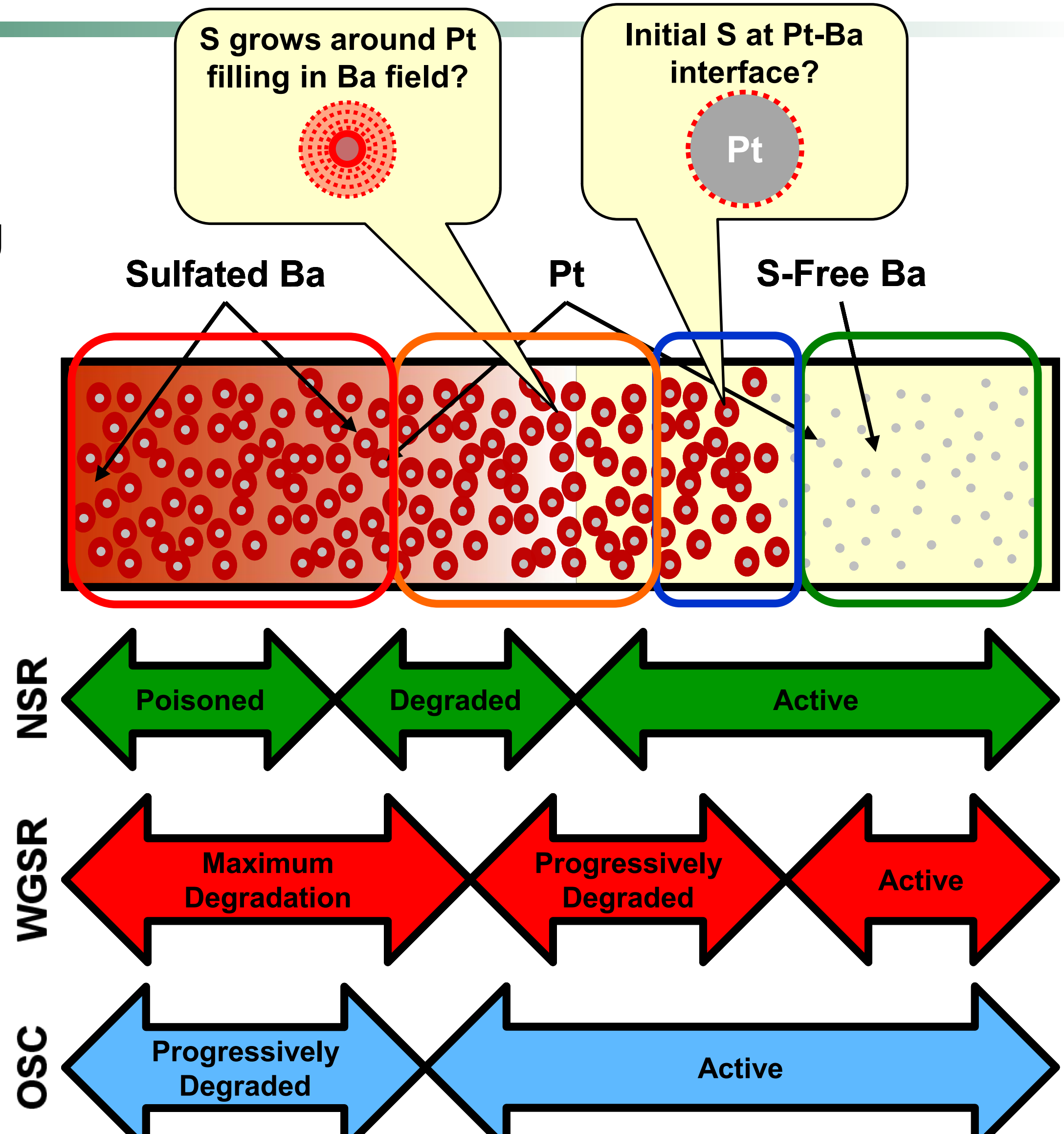
- ***Suggests inhibiting $NH_3$ & NO interactions not impacted by FA***
  - *Abundance of S2 vs S1 sites*
    - *i.e., $NH_3$ spillover from S2 to S1 is equivalent in DG & FA; even with lower FA TC*
    - *Consistent with lower $NH_3$ vs. NO capacity*
    - *Consistent with separate S1 & S2 sites*
    - *Can lose many S2 sites before change in NO-adsorption inhibition occurs*
    - *FA selectively impacts S2 sites over S1?*

# Remaining Challenges & Barriers, and Proposed Future Work

| **Remaining Challenges:** | **Future Work (FY2015; i.e., from 2014 AMR):** |
|---|---|
| • Characterize distributed impact of ageing on SCR-catalyst functions & performance | ✔ Study HydroThermally Lab-Aged sample<br>✔ Complete experimental matrix & analysis<br>- DeG & HTAged 2010CMI SCR samples<br>- Standard & Fast SCR<br>- 200, 300 & 400°C |
| • Resolve $NH_3$ Capacity distributions via transient analysis<br>- Resolve Dynamic-, Unused- & Total-Capacity | ✔ Determine capacity distributions using an improved transient analysis method incorporating instrument isotherms |
| • Understand mechanisms of ageing-induced performance degradation<br>- Mine insights for improving catalyst development models & control | ✔ Correlate impacts of Temp., SCR Reaction & Ageing on distribution of specific functions<br>- E.g., further work as presented here<br>In process • Comparison of measurements to SCR models<br>- Assess model performance and sensitivity vs. specific parameters, ageing and functions<br>✔ Continue University collaborations |
| • Advance detailed understanding of ageing<br>- Impacts of degree of ageing<br>- Impacts of different real-world conditions | ✔ Similar studies on catalyst in other aged states<br>- Further HT Lab Ageing<br>- Field-aged 2010CMI catalyst samples |

# Conceptual Model of Sulfur Impact on NSR, WGS & OSC

- **Fully active in S-free zone**
- **WGS sensitive to initial S**
- **$O_2$ keeps Pt S free in fast cycling**
- **S-islands grow around Pt sites**
  - Progressive WGS degradation
  - NSR insensitive to initial S
    - S-free Ba exists in field
  - Progressive NSR degradation
  - WGS degradation max
  - Field sulfation begins
- **Field sulfation continues**
  - NSR becomes poisoned
  - Progressive minor OSC loss
    - Due to minor Ba-peroxide?
- **WGS S-front leads NSR S-front**
  - No regeneration from WGS $H_2$

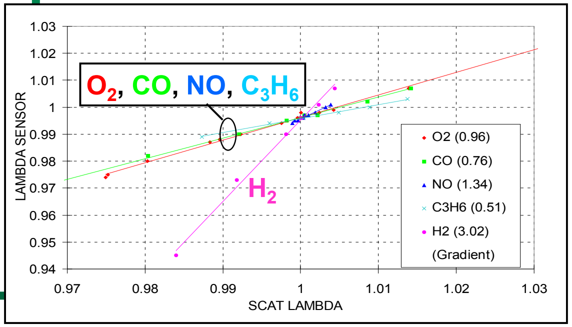



*Ex. of fundamental insights from laboratory SpaciMS-based studies; nxt. pg. shows how such fundamental insights can be used to achieve practical OBD advances.*

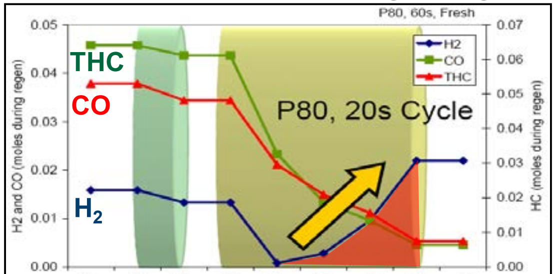
# Ex. Practical OBD Based on Fundamental Catalyst Insights

- **Need to minimize high-T DeS events**
  - Basic control commands DeS too often and too long
- **WGS enables advanced control**
  - Cummins OBD Patent (US Patent App. 20080168824)
  - Active on-board assessment of catalyst state
  - Only DeS when & for as long as required
    - Better efficiency (lower fuel penalty)
    - Better durability (catalyst & engine last longer)

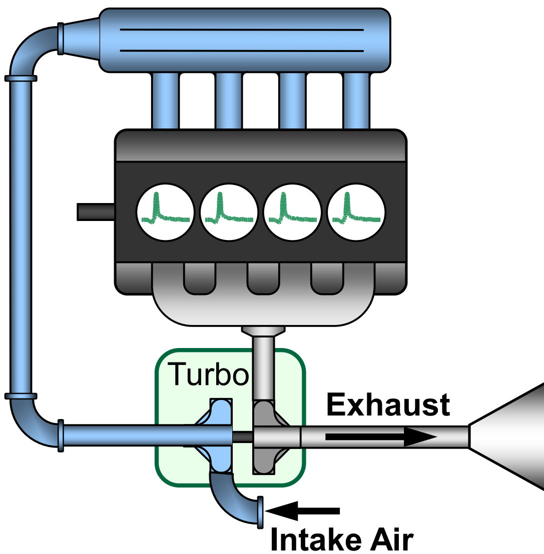
UEGO has unique $H_2$ cross sensitivity

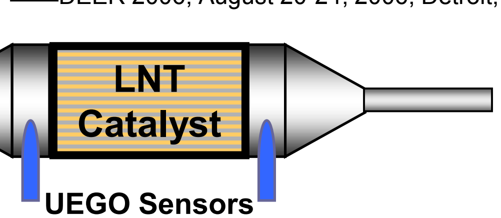



LNT WGS α Ageing

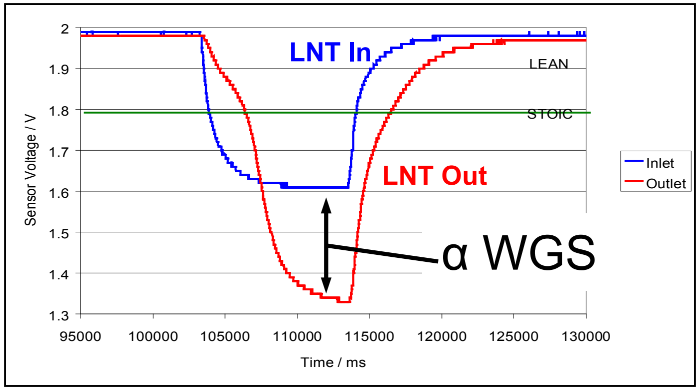



Parks, Swartz, Huff, West. ORNL.
DEER 2006, August 20-24, 2006, Detroit, MI

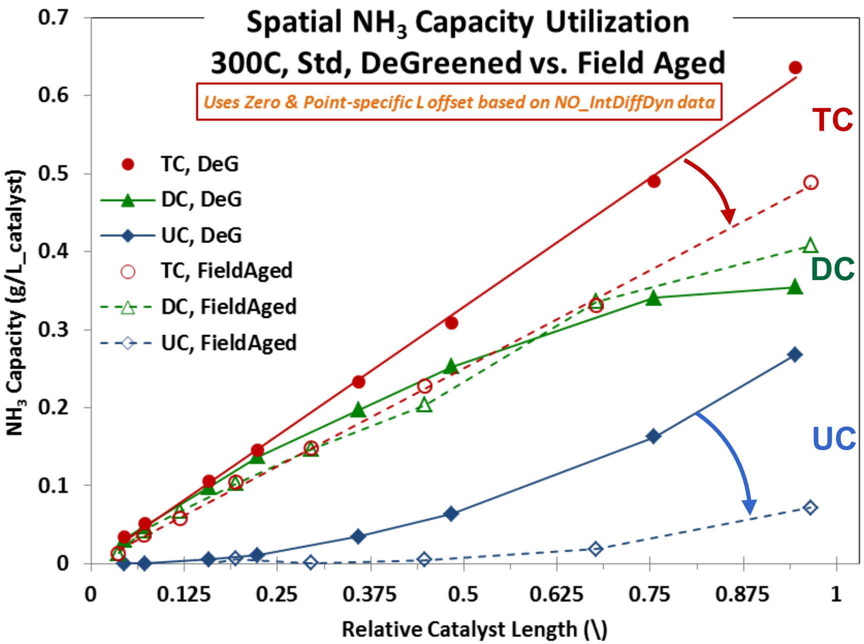


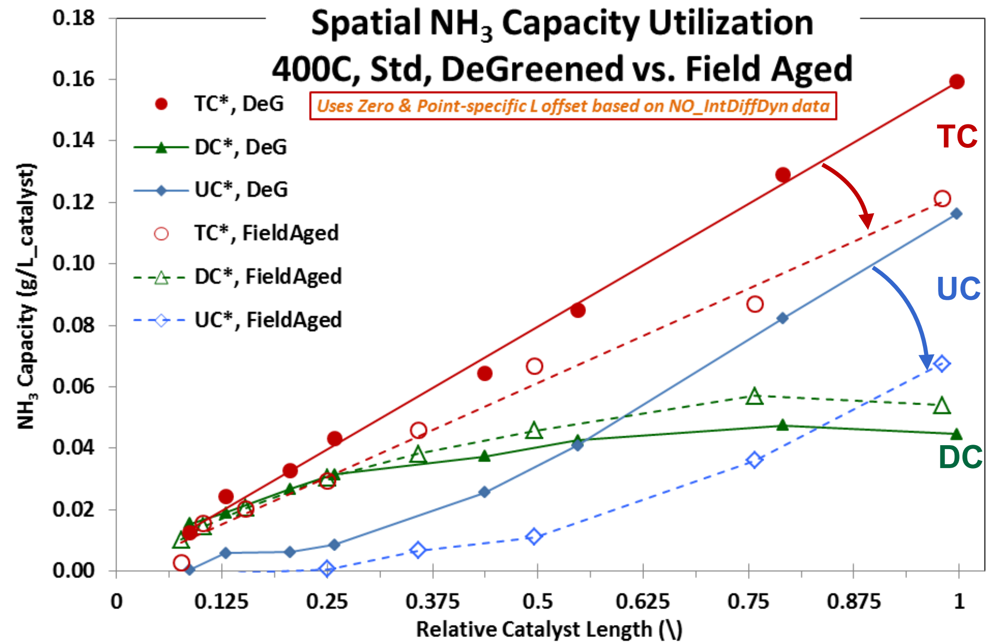




UEGO Signal α WGS



## Tech.Prog.: Field Ageing Changes TC & UC, but Little DC Impact



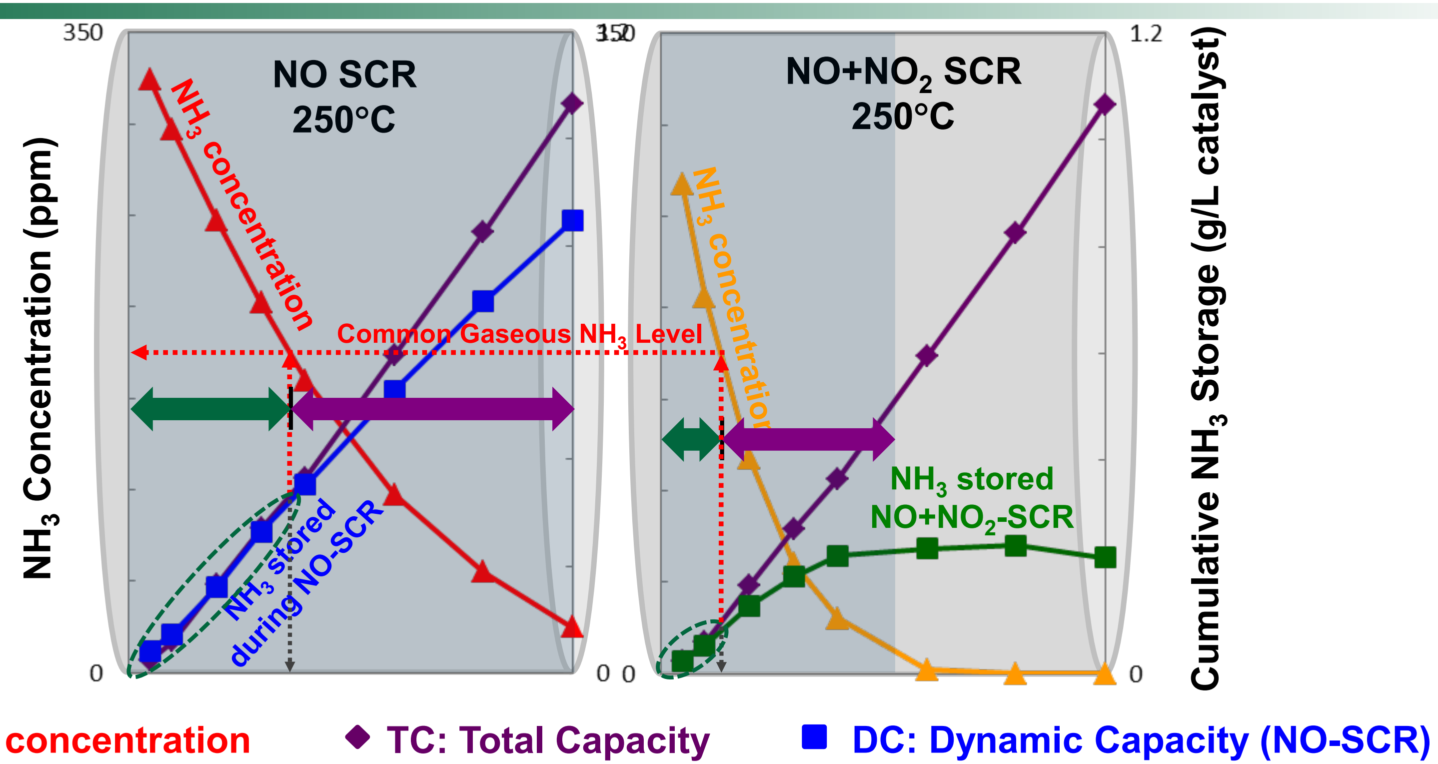




- Total $NH_3$ Capacity: **TC**
  - FA ~25% lower at both 300 & 400°C
- Dynamic $NH_3$ Capacity: **DC**
  - DC≈TC at catalyst front
  - FA causes DC≈TC deeper into catalyst
    - Due to TC pivoting down
    - DC saturated deeper into catalyst
    - $[NH_3]$ similar at DC-TC separation point
      - Suggests similar Adsorption Isotherm

- Unused $NH_3$ Capacity: **UC**
  - FA lowers UC
    - Due to TC & DC behavior
  - May impact dosing control
- Same general behavior at 400°C
- ***Little impact of FAgeing on DC does not correlate with large SCR loss***

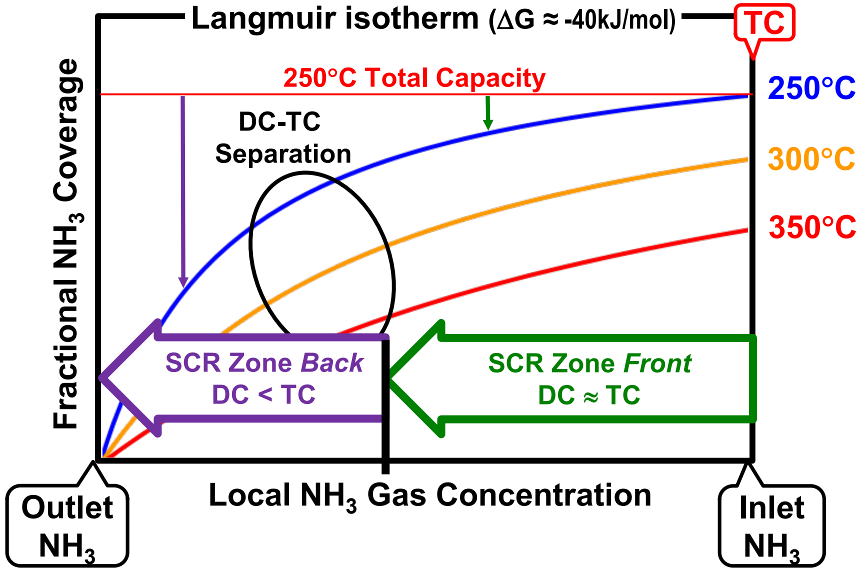
**DC + UC = TC**

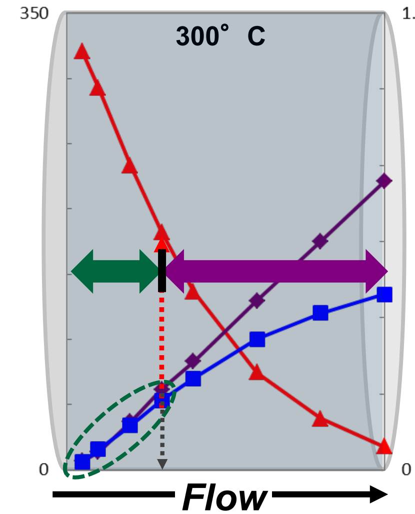
# $NH_3$ Coverage Equilibrium is Faster than Even Fast SCR




- Three DC-vs.-TC zones: ***Equal***, ***Separation***, ***Lower***
- DC ≈ TC in catalyst front section where $NH_3$ is high
- DC < TC in back of SCR zone
- DC ≈ TC above the ***same common ~175 ppm $NH_3$ level***
  - A case where NO & NO+$NO_2$ SCR are similar!
  - $NH_3$ coverage equilibrium reactions much faster than NO+$NO_2$ SCR

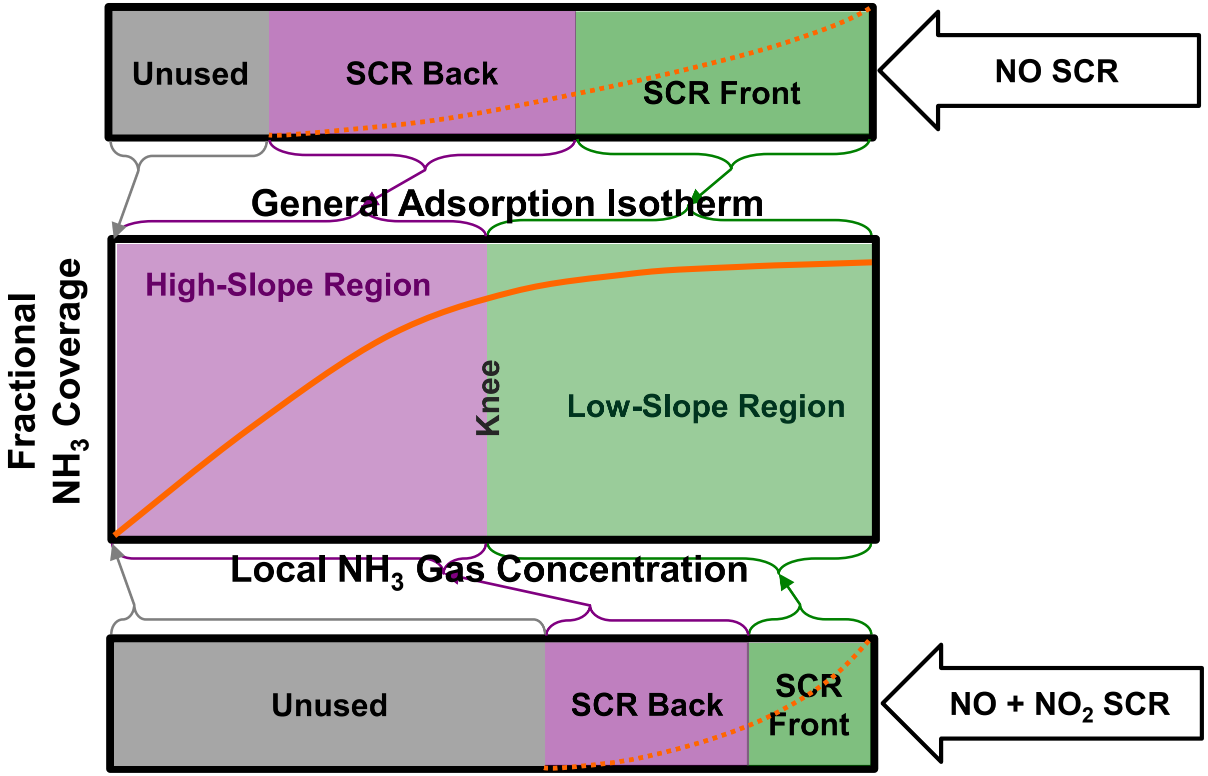
# Isotherm & Gas-Phase $NH_3$ Distribution Set $NH_3$ Coverage Distribution




- Adsorption isotherm indicates equilibrium-coverage variation with $NH_3$
  - TC measured at inlet $NH_3$
  - 3 major zones: **low-slope**, **knee** & **high-slope**
- Coverage variation is relatively flat in low-slope (high-$NH_3$) zone
  - practically: DC ≈ TC here
- DC & TC should separate around the isotherm knee $NH_3$ concentration
- DC<TC in high-slope zone corresponding to SCR-zone back
  - local $NH_3$ & coverage going to zero here
- Specific SCR reaction does not change the isotherm
  - only changes where these zones occur spatially within the catalyst

# Major Isotherm Zones can Move within the Catalyst




- Specific SCR Reaction, SV, etc. can change the $NH_3$ distribution
  - Spatial applicability of different isotherm zones (**low-slope**, **knee** & **high-slope**)
- Isotherm & local $NH_3$ determine the local coverage
- But local $NH_3$ is also dependent on local coverage
  - Rate coefficient & coverage are both temperature dependent
  - Creates complex distributed behavior
- Actual catalysts can have more complex adsorption-isotherm shape
  - Further complicating distributed performance, temperature dependence, etc.